Electro–optic Studies on Polymer-Dispersed Liquid Crystal Composite Films. I. Composites of PVB–E7

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ABSTRACT: The electro-optic performance characteristic of polymer-dispersed liquid crystal (PDLC) composite films out of poly(vinyl butyral) (PVB) and nematic liquid crystal (E7) have been studied for a wide range of PVB–E7 composite compositions (20–70 wt % of E7). Composites were prepared by solvent casting from chloroform at room temperature. A scanning electron microscopy study showed that a E7 phase is continuously embedded in chink-like structure of PVB matrix. Optical transmittance of the composite films (of 60 and 70 wt % loading of E7) under an alternating current (ac) electric field (0–250, $V_{p\text{-}p}$) and frequency (50 Hz to 1 KHz) were measured employing He—Ne laser (λ = 632.8 nm). The results indicate that the (PVB–E7) composite exhibits a memory effect. In the memory state, higher transmittance is preserved without applying voltage. The memory state can be erased and changed to the scattering Off-state by heating the film to the clearing temperature of the liquid crystal. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 3485–3491, 1999

Key words: poly(vinyl butyral); nematic liquid crystal (E7); polymer-dispersed liquid crystal; PDLC composite; memory effect; thermal addressing; display device

INTRODUCTION

Interest in exploiting the unique electro-optical effect of the polymer and/or liquid crystal (LC) composite film based on the light scattering and/or light switching has gained tremendous importance during the last two decades.[1–6] Since these composite films possess good mechanical properties and processing ease, they are being investigated, particularly as flexible, large-area electro-optical devices.[3] In addition, the high electrical response on the order of a few milliseconds observed under an ac electric field and enhanced transmitted light with a wide-angle viewing cone, are added advantages over twisted nematic-type devices. However, these optimized functional responses are highly dependent on the optical microstructural heterogeneties and/or homogeneties of the composite film[4] and the hydrodynamic properties of the LC molecules. These optical states in the composite correspond to the modulated, external-electric-field-induced, random, unidirectional orientation of LC director. Hence, the resulting electrooptical phenomenon can be attributed to the mismatch of the refractive indices between polymer and LC phase. Kajiyama[4] proposed that the spatial distortion of nematic directors in the distorted, LC, continuous channel also contribute to optical heterogeneity. Therefore, the order of light scattering is highly dependent on the shape and size of the LC droplets, its compatibility with the matrix polymer, and other optical parameters, such as refractive index and the birefringes. This article presents the electro-optical properties of the PVB–E7 composite films (PDLC) fabricated by the solvent-induced phase separation (SIPS) method.
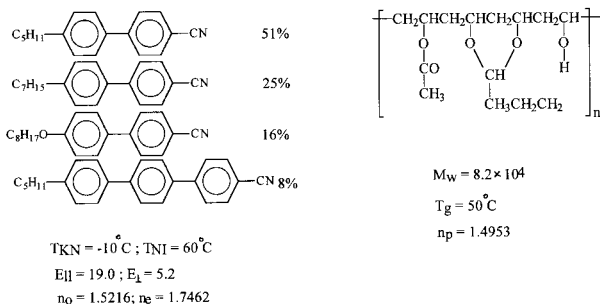
Figure 1 Chemical structure and physical properties of polymer matrix (PVB) and liquid crystal (E7).

EXPERIMENTAL

Materials

The thermotropic nematic liquid crystal (E-7) used in present studies is a eutectic commercial mixture of cyanophenyl derivatives [4-alkyl or (4-alkyloxy)-4 cyanobiphenyl and 4-alkyl-4′-cyanotriphenyl] obtained from E. Merck, UK. It exhibits positive dielectric anisotropy. Poly(vinyl butyral) (PVB) (obtained from Amrut Industrial Products, India) was used as matrix polymer. The chemical structures and physical properties of the matrix polymer and LC for the composite films are shown in Figure 1.

Preparation of the Composite Film

The SIPS technique for preparing PDLC films was applied.[1,2] The composite films of a different composition of polymer and LC were prepared from homogeneous solution of an appropriate amount of a LC (E7) and a polymer (PVB) in chloroform (AR grade) by spreading over indium–tin oxide (ITO)-coated glass at room temperature. The solvent evaporation rate during a film preparation process was controlled to get an identical aggregation structure. The composite film was sandwiched between two indium-ITO-coated glass plates (dimensions 6×6 mm), which were separated by a polyethylene terephthalate film spacer to control composite film thickness (10 ± 2 μm).
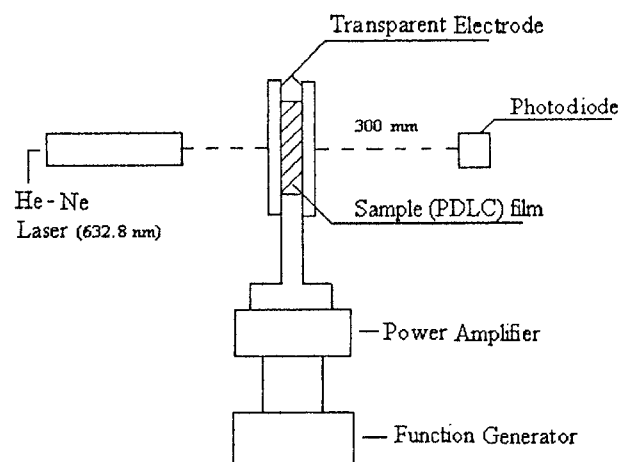
Morphology

Morphologies of the composite films were studied using a scanning electron microscopy (SEM, Cambridge Stereoscan 150). LC molecules were first extracted in n-hexane at 28°C, and the films were dried overnight under vacuum. The weight loss upon extraction was used to decide the continuity of LC domains in polymer matrix. When the LC domains are interconnected in three dimensions, almost all of the LC that was initially loaded was extracted. The dried films were cryogenically (in liquid nitrogen) fractured and sputtered with gold before viewing under SEM. Also, the microstructure (director configuration) of the LC composite film was viewed through a polarizing microscope (Carl Zeiss, Trinocular Research microscope, AXIOLAB-100).

Electro-optic Measurements

Electro-optical switching characteristics of the composite films were measured by a setup shown schematically in Figure 2. A collimated beam of polarized He—Ne laser (5 mW power at wavelength 632.8 nm, Photochemical Research Inc. Canada, model 105 P) was used as a incident light source. The transmitted light intensity without any polarizer was measured under the modulation of an ac electric field in normal transmission geometry employing a photodiode (Jain Lasertech, India). The amplified variable ac square wave voltage generated by function generator (Systronics, Wideband oscillator, 1002, India) (0–240 $V_{p\text{-}p}$) at different frequencies (50, 100, and 500 Hz 1 and 5 KHz) has been applied to the drive shutter. The response of the photodiode was monitored with a digital storage oscilloscope (Aplab 50 MHz, 3538, India). The distance between the cell and photodiode was 300 mm.

Figure 2 Schematic diagram of the experimental setup.
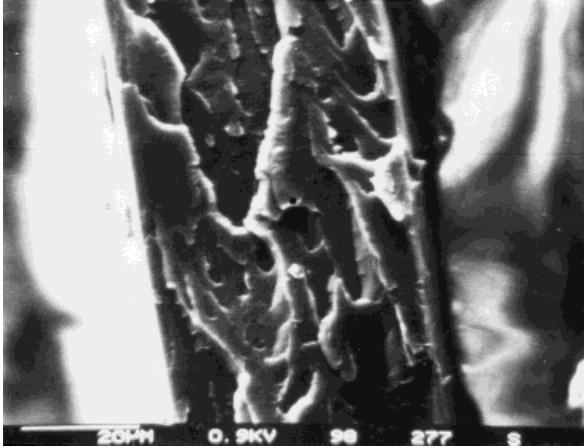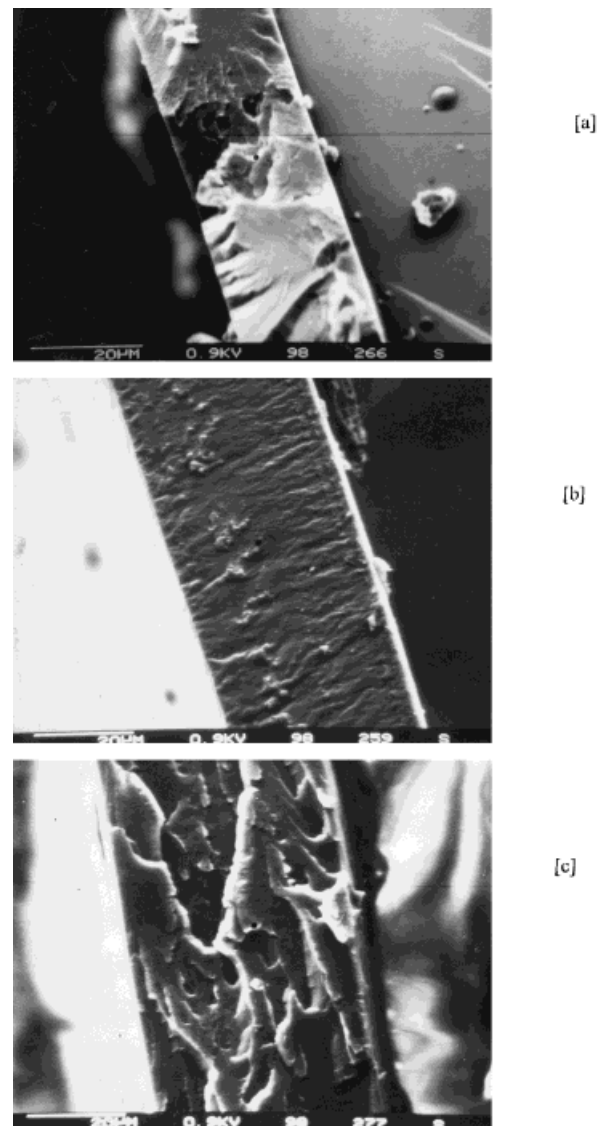
Figure 3 SEM micrograph of 40/60 film.

## RESULTS AND DISCUSSION

Morphology

Morphology of the dispersed domains depends on a number of factors, such as the materials used to form the film, the composition, and, in particular, on the details of the film formation procedure.[3] In SIPS, the shorter the evaporation time allowed, the less that coalescence occurs resulting in droplet-dispersed domains. However, in the present PVB–E7 system, even with the shortest evaporation time experimentally possible to us, the films obtained were with continuous phase rather than dispersed droplets. For the present studies, composite films of different compositions of polymer–LC (PVB–E7) with identical thickness (10 ± 2 μm), prepared under the same conditions and rate of evaporation, were used.

Figure 3 shows the SEM micrographs of the dried composite film (40/60 wt % PVB–E7), taken after extracting LC with n-hexane, which is, however, a nonsolvent for polymer matrix, for 12 h. The weight loss upon extraction can be used to decide the continuity of LC domains in polymer matrix. As the weight change of the composite films after extracting LC almost corresponded to the loaded LC weight fraction, respectively, it clearly indicates that almost all of the LC fraction in the composite films were possible to extract. Therefore it is apparent that in the composite films of PVB–E7, the polymer (PVB) forms three-dimensional spongy, chink structures, observed as the combination of more or less curved and stratified crack structures[5] in which the LC (E7) domains are embedded. Since the LC has significantly lower viscosity than matrix polymer, the

LC domains show phase-separated, continuous, elongated structures. It is observed that with increasing LC loading in composite (Fig. 4), the number of these structures formed out of the coalescing process of LC domains increases, which eventually leads to formation of continuous LC channels embedded in polymer matrix. The 40/60 and 30/70 wt % composites exhibit an almost similar morphology with, to some extent, a better coalescing process. With such a morphology, it seems reasonable to consider that the present composite films of 40/60 and 30/70 wt % compositions can be treated as a binary dielectric composite composed of two different dielectrics (polymer

Figure 4 SEM micrographs of different compositions (a) 80/20, (b) 60/40, and (c) 40/60.
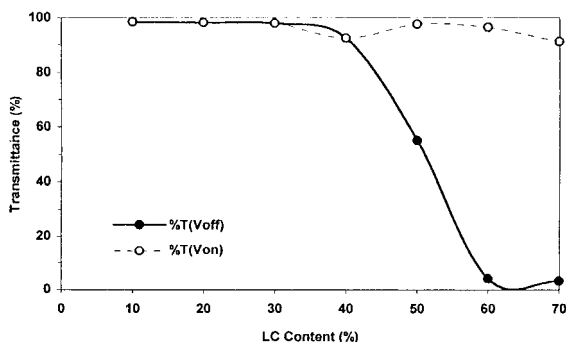
Figure 5 Optical contrast of (PVB–E7) films versus LC content (power corresponds to 1 KHz, 200 $V_{p\text{-}p}$, and 28°C).

matrix and LC). This structural heterogeneity corresponds to the source of optical heterogeneity for the composite in the off-state of an external field.

Effect of LC Loading

Figure 5 shows the off- and on-state (1 KHz, 200 $V_{p\text{-}p}$) transmittance of the film of varying LC contents measured at ambient temperature (28°C). The dramatic decrease of transmittance for ≥ 50 wt % LC loading in composite film indicates that the formation of continuous, three-dimensional LC channels out of a dense chink-structure, is important for light scattering (Fig. 4). These LC channels are interconnected through fibril morphology of matrix polymer and induce the strong spatial distortion of nematic directors upon an electric field off-state.[4,6] It is further observed that the on-state transmission is practically constant and is the order of 95%. This is predominantly due to the applied electric-field-induced positive dielectric anisotropy along the long axes of LC molecules, thus leaving no scattering sites. Considering composites for optical application with high contrast as well as high on-state transmittance,[7] the films loaded with 60 and 70 wt % are most valuable (Fig. 6); thus further, the electro-optic responses with ac electric voltages have been studied for these two compositions. The films with ≥ 80 wt % loading exhibit poor adhesion problem.

Voltage Dependence of Transmittance

Figure 7 shows the transmittance change as a function of the applied voltages at various frequencies. Initially, the transmittance increases slowly with voltage up to approximately 40 $V_{p\text{-}p}$
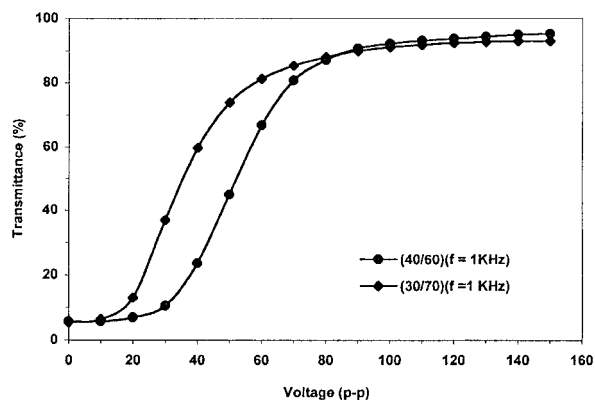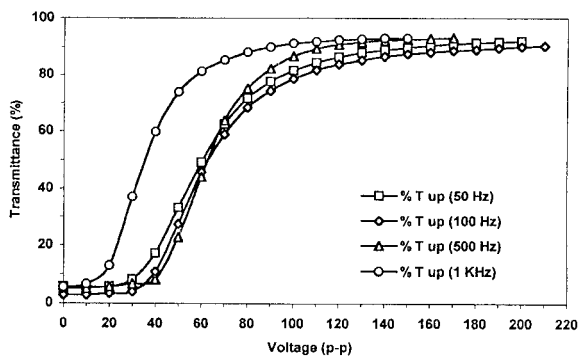

Figure 6 Effect of LC loading on threshold voltage (V_{th}) of composite.

and then increases drastically in the range of 40–90 $V_{p\text{-}p}$. The observed threshold voltage (V_{th}) for 60 and 70 wt % composite are 30 and 20 $V_{p\text{-}p}$, at 1 KHz, respectively.
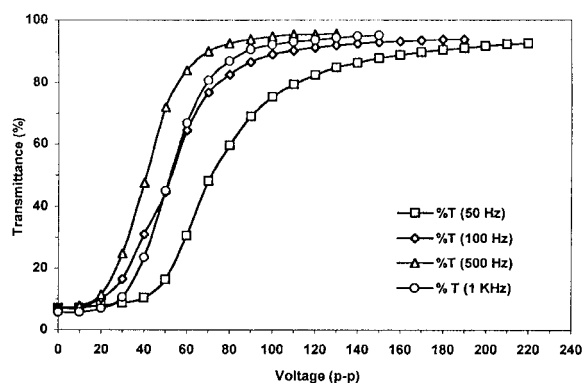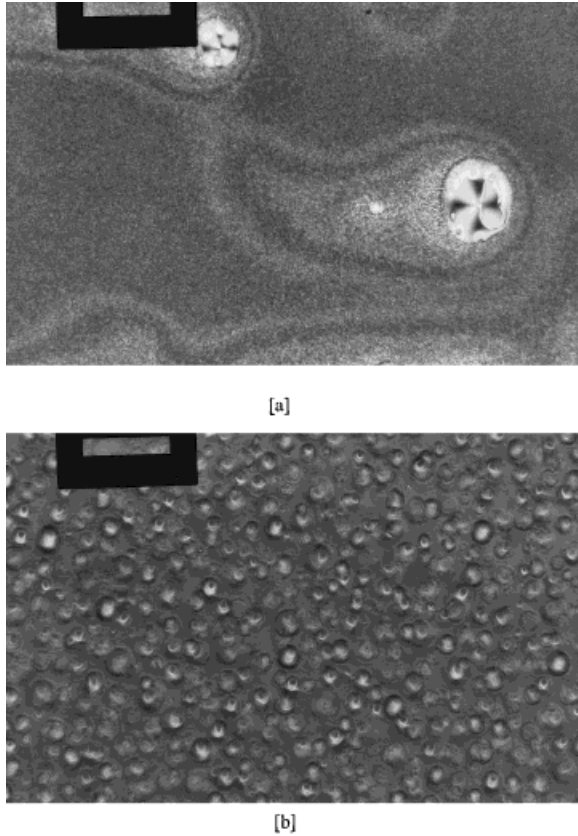

[a]

[b]

Figure 7 Transmittance as function of $V_{p\text{-}p}$ at various frequencies (a) 40/60 and (b) 30/70.

Figure 8 Polarizing micrograph for (PVB–E7) (40/60) (a) with and (b) without polarizer.

It should be mentioned that the transmittance response with voltage in Figure 7 corresponds to high frequency characteristics. In a high frequency range, molecular orientation cannot follow a superposed electric polarity change, and the transmittance output varies in a fashion of simple monotonic (not periodic) asymptote.[1] However, in a low frequency range, a periodic flicker of transmitted light with twice of imposed frequency overlapping the asymptote was observed.[4]

The transmittance of powered film depends on average orientation of nematic directors, which is determined by the balance between electric and elastic torque. The elastic torque consists of splay, twist, and bend deformations and depends on the director configuration.[4] Consequently, V_{th} depends on the director configuration. In this (PVB–E7) system polarizing microscopy, Figure 8 shows the bipolar configuration of LC director.

As mentioned earlier, we found that in all PDLC cells the transmission at fixed applied voltage increased significantly with increasing frequency, reaching a maximum at frequencies near

a few KHz. Electro-optic response of the PDLC cell (Fig. 7) is best around 500 Hz and 1 KHz. This, in turn, implies that the actual voltage appearing across the droplets should be minimum around that frequency. These results can be best understood in terms of the dielectric response of PDLCs.[8,9] These studies have shown that in a PDLC mixture with $\rho_p > \rho_{LC}$ (ρ_p and ρ_{LC} are the resistivities of the polymer and liquid crystal, respectively) and at low frequencies, the space charge buildup at the LC droplet–polymer interface results in a strong increase in the dielectric permittivity of the mixture. This should greatly reduce the voltage that appears across the LC droplet and, thus, should lead to high values for the threshold voltage. Since the space charge buildup decreases with increasing frequency because the charge cannot follow the field at frequencies above a few KHz, we may expect a decrease in the threshold voltage with increasing frequency. The threshold voltage (V_{th}) is defined as voltage to raise the transmittance by 10% is smaller for 70 wt % LC loading than for 60 wt % LC (Fig. 6).

The higher field requirement of film with low LC loading is consistent with general trends reported by others[6,10] and is predictable from the polymer–LC series model.[6] For comparable droplet size bipolar configuration, which occurs in most cases, V_{th} is substantially less than in alphabet configuration,[3,11] as given by

$$V_{th} = \frac{d}{3a}\left(\frac{\rho_P}{\rho_{LC}} + 2\right)\left(\frac{K(l^2 - 1)}{\varepsilon_0 \Delta \varepsilon}\right)^{1/2}$$

where d, a, ρ, K, and l represent film thickness, major dimension, resistivity, elastic constant, and aspect ratio, respectively. With larger sections, the polymer–LC interfacial area becomes smaller, leading to smaller total interfacial energy requirement for director alignment. These factors contribute physically to lower the V_{th} of 70 wt % LC film.

Memory Effects

Figure 9(a) and (b) shows transmission properties of 40/60 and 30/70 (polymer–LC) composite films at various frequencies for reducing voltage. After reaching saturation voltage (V_{th}), the voltage across the film is reduced gradually, but films continue to show higher transmittance after voltage application (memory state) than those in their initial Off-state. It has been observed that
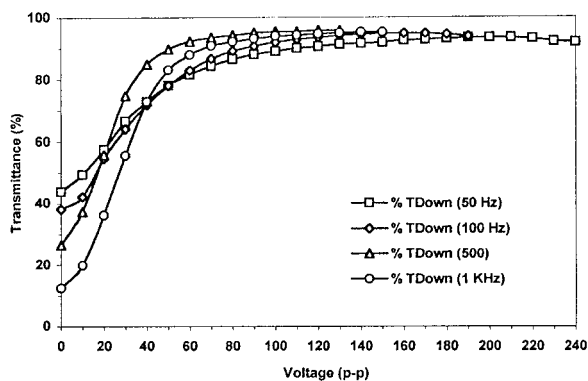
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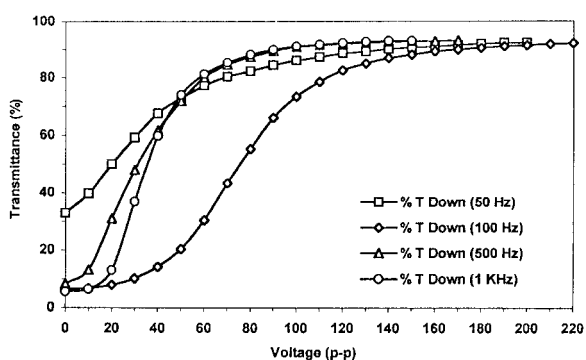
[b]

Figure 9 Transmittance as function of reducing $V_{p\text{-}p}$ at various frequencies (a) 40/60 and (b) 30/70.

this (memory state) transmittance of the film decreases with increasing frequency. This may be due to, with increasing frequency, the boundary condition at the interface between the LC and the PVB matrix might be changing due to thin layers of matrix polymers.

Memory states of these two films are maintained for more than several weeks at room temperature. These observations may be attributed to the partial alignment of LC molecules along the direction of the electric field even in the off-state.[5] In this memory state, the effective refractive index of the liquid crystal is still closer to the that of the polymer matrix, and the PDLC film preserves a transparent state. In addition, the heat generated due to dielectric dissipation may induce the structural change in PDLC film after the saturation voltage and above the clearing temperature, which is 60°C for E7. Since in most cases of the polymer–LC composites, LC acts as plasticizer for polymer, LC provides the composites with flexi-

bility.[12–16] As in the present case, even at 10 wt % of E7 loading, lowers the glass transition temperature of PVB from 50°C to 38°C (Fig. 10) (obtained by employing a Stanton Redcroft differential thermal analyzer STA 780), sufficiently below the clearing temperature, the heat generated by dissipation will be subsequently enough to alter the polymer matrix in 60 and 70 wt % of LC loading and PDLC films preserve a transparent state. However, in the present case, due to the lack of facility, it was not possible to locate the actual glass transition temperature of 40/60 and 30/70 composites as it will shift in the subambient temperature region. These possible structural changes induce a greater disorder of the bipolar orientation, which takes a longer time duration creating memory states. At such a situation, the increased polymer flexibility resulting out of plasticizing effect in the composite, might allow the droplets on the chink structures to relax from elliptical (nonuniform) to a more spherical (uniform) shape.[12–16] This relaxation could result from the relief of stored up strain in the polymer. These memory states can be erased and the initial scattering off-state can be attained by reheating the film up to clearing temperature of the liquid crystal.

CONCLUSION

A new type of memory effect of light transmission properties in the PDLC was described. In the memory state, higher transmittance of the film is preserved without applying voltage, compared to those in the initial off-state. From the SEM photographs, PDLC films with large memory effects have no microdroplets but have a structure with many chinks containing liquid crystal. The mem-
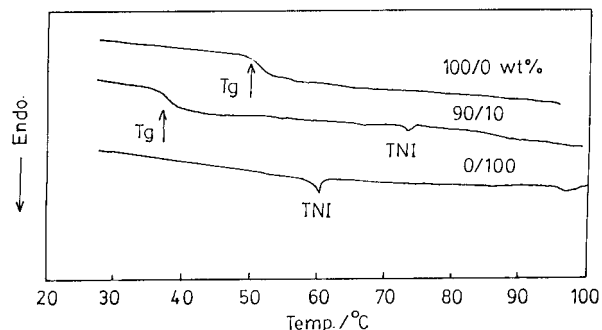
Figure 10 DTA curves of the PVB (100/0 wt %), PVB–E7 (90/10 wt %), and E7 (0/100 wt %).

ory state can be erased and the initial off-state can be attained by heating the film up to the clearing temperature of the liquid crystal. PDLC films with memory effects can be applied to display devices, for example, thermally addressed light valves.

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